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Abstract

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[Title of the Invention]

SYNTHETIC RESIN EMULSION POWDER AND ITS USE

[Claims]

1. A synthetic resin emulsion powder obtained by spray-drying an emulsion (A) where the dispersant is a polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units with at most 4 carbon atoms and the dispersoid is a polymer having one or more unsaturated monomer units selected from ethylenic unsaturated monomers and dienic monomers.

2. The synthetic resin emulsion powder as claimed in claim 1, wherein the  $\alpha$ -olefin units are ethylene units.

3. The synthetic resin emulsion powder as claimed in claim 1 or 2, wherein the content of the  $\alpha$ -olefin units is from 1.5 to 15 mol%.

4. The synthetic resin emulsion powder as claimed in claim 1 or 2, wherein the content of the  $\alpha$ -olefin units is from 2 to 12 mol%.

5. The synthetic resin emulsion powder as claimed in any of claims 1 to 4, wherein the polymer having one or more unsaturated monomer units selected from ethylenic unsaturated monomers and dienic monomers is a polyvinyl ester or an olefin-vinyl ester copolymer.

6. The synthetic resin emulsion powder as claimed in any of claims 1 to 5, which is obtained by mixing from 1 to 50 parts

by weight, relative to 100 parts by weight of the solid content of the emulsion (A), of a polyvinyl alcohol (B) to the emulsion (A) followed by spray-drying the resulting composition.

7. The synthetic resin emulsion powder as claimed in claim 6, wherein the polyvinyl alcohol (B) contains, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units.

8. The synthetic resin emulsion powder as claimed in any of claims 1 to 7, wherein the polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units with at most 4 carbon atoms has from  $(1.7 - X/40)$  to 4 mol% of 1,2-glycol bonds in which X (mol%) indicates the olefin unit content of the polymer.

9. The synthetic resin emulsion powder as claimed in any of claims 1 to 8, which contains an inorganic powder.

10. An additive or joint material for hydraulic substances, which comprises the synthetic resin emulsion powder of any of claims 1 to 9.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to synthetic resin emulsion powder and to additive or joint material for hydraulic substances that comprises the emulsion powder. More precisely, the invention relates to synthetic resin emulsion powder obtained by spray-drying an emulsion where the dispersant is a polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin

by weight, relative to 100 parts by weight of the solid content of the emulsion (A), of a polyvinyl alcohol (B) to the emulsion (A) followed by spray-drying the resulting composition.

7. The synthetic resin emulsion powder as claimed in claim 6, wherein the polyvinyl alcohol (B) contains, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units.

8. The synthetic resin emulsion powder as claimed in any of claims 1 to 7, wherein the polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units with at most 4 carbon atoms has from  $(1.7 - X/40)$  to 4 mol% of 1,2-glycol bonds in which X (mol%) indicates the olefin unit content of the polymer.

9. The synthetic resin emulsion powder as claimed in any of claims 1 to 8, which contains an inorganic powder.

10. An additive or joint material for hydraulic substances, which comprises the synthetic resin emulsion powder of any of claims 1 to 9.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to synthetic resin emulsion powder and to additive or joint material for hydraulic substances that comprises the emulsion powder. More precisely, the invention relates to synthetic resin emulsion powder obtained by spray-drying an emulsion where the dispersant is a polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin

units with at most 4 carbon atoms and the dispersoid is a polymer having one or more unsaturated monomer units selected from ethylenic unsaturated monomers and dienic monomers, and to additive or joint material for hydraulic substances that comprises the emulsion powder.

[0002]

[Prior Art]

Synthetic resin emulsion powder is produced by spray-drying a synthetic resin emulsion, and is superior to the starting emulsion thereof in point of the processability and the transportability as it is powdery. Before use, water may be added to the powder and stirred, whereby the powder may readily redisperse in water. Accordingly, the powder is much used in various applications for additives to cement and mortar, adhesives, binders for coating compositions, etc. In particular, since the powder can be premixed with mortar to realize various modifications of commercial products, and it is especially favorable for additives to mortar and is therefore widely used in the art. However, when conventional synthetic resin emulsions are directly spray-dried, then the dispersoid particles therein may readily fuse together and could not redisperse in water. At present, therefore, a large amount of polyvinyl alcohol must be added later to the emulsions, or a large amount of inorganic powder such as silicic anhydride that serves as an antiblocking agent must be in the emulsions to solve

the problem. Used is a powder that is obtained by spray-drying an emulsion with a mercapto-terminated polyvinyl alcohol serving as a dispersant (patent reference 1). Known is a powder that is obtained by spray-drying an emulsion with a 1,2-glycol bond-rich PVA which is prepared through high-temperature polymerization and serves as a dispersant (patent reference 2). The redispersibility of these synthetic resin emulsion powders is good, as in Comparative Examples 6 to 7 given hereinunder, but is not still satisfactory. For example, when the powders are used as additives to cement mortar, the mechanical strength of the resulting cement mortar is not always satisfactory.

[0003]

[Patent Reference 1]

JP-A 9-151221, claims and paragraphs [0011] and [0020]

[Patent Reference 2]

JP-A 2001-342260, claim 1

[0004]

[Problems that the Invention is to Solve]

An object of the invention is to solve the problems as above and to provide synthetic resin emulsion powder of good redispersibility, of which the redispersion has good film formability and which, when used as an additive or joint material for hydraulic substances, gives hardened constructions of high strength.

[0005]

[Means for Solving the Problems]

Considering the situation as above, we, the present inventors have assiduously studied and, as a result, have found that the above problems can be solved by a synthetic resin emulsion powder obtained by spray-drying an emulsion (A) where the dispersant is a polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units with at most 4 carbon atoms and the dispersoid is a polymer having one or more unsaturated monomer units selected from ethylenic unsaturated monomers and dienic monomers, and that, when the powder is used as an additive or joint material for hydraulic substance, it gives hardened constructions of high strength. On the basis of this finding, we have completed the present invention.

[0006]

[Modes of Carrying out the Invention]

The synthetic resin emulsion powder and the additive or joint material for hydraulic substances of the invention are described in detail hereinunder.

The polyvinyl alcohol which serves as the dispersant in the emulsion (A) and which contains, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units with at most 4 carbon atoms may be obtained through hydrolysis of a copolymer of a vinyl ester and an  $\alpha$ -olefin with at most 4 carbon atoms. The  $\alpha$ -olefin units with at most 4 carbon atoms include ethylene, propylene, butylene and isobutylene units, and ethylene units are the best. The



reason why ethylene units are the best is obvious from Examples mentioned hereinunder.

It is a matter of importance that the polyvinyl alcohol contains from 1 to 20 mol% of  $\alpha$ -olefin units such as typically ethylene units. Preferably, the  $\alpha$ -olefin unit content is at least 1.5 mol%, more preferably at least 2 mol%. Also preferably, the content is at most 15 mol%, more preferably at most 12 mol%. If the content of  $\alpha$ -olefin units such as typically ethylene units lower than the range, the redispersibility of the emulsion powder is not good and the strength of the hardened constructions such as cement mortar containing the emulsion powder could not be satisfactorily high, as is obvious from Comparative Example 4 given hereinunder; but if higher than the range, good emulsion powder could not be obtained, as is obvious from Production Example 12 given hereinunder.

[0007]

One preferred embodiment of the polyvinyl alcohol that contains from 1 to 20 mol% of  $\alpha$ -olefin units for use in the invention has a 1,2-glycol bond content at least  $(1.7 - X/40)$  mol% in which X (mol%) indicates the  $\alpha$ -olefin unit content of the polymer. Using the polymer of the preferred type further improves the redispersibility of the emulsion powder obtained herein.

For producing the polymer of the type, for example, employable is a method of copolymerizing vinylene carbonate with

ethylene in such a controlled manner that the 1,2-glycol bond content of the resulting copolymer could fall within the range as above; or a method of copolymerizing ethylene and a vinyl ester under pressure in such a controlled manner that the polymerization temperature is kept higher than usual, for example, falling between 75 and 200°C. Though not specifically defined, the polymerization temperature in the latter method may generally fall between 70 and 190°C, preferably between 75 and 160°C.

[0008]

In this case, the 1,2-glycol bond content is preferably at least  $(1.7 - X/40)$  mol%, more preferably at least  $(1.75 - X/40)$ , most preferably at least  $(1.8 - X/40)$ . Also preferably, the 1,2-glycol bond content is at most 4 mol%, more preferably at most 3.5 mol%, most preferably at most 3.2 mol%. The 1,2-glycol bond content of the polymer may be obtained through NMR spectral analysis thereof.

[0009]

The viscosity-average degree of polymerization (hereinafter abbreviated to "degree of polymerization") of the polyvinyl alcohol may be suitably determined in accordance with various conditions, not specifically defined. For easy operation to powder the emulsion, in general, it may be preferably from 100 to 3000, more preferably from 150 to 2000, even more preferably from 200 to 1600, most preferably from 200 to 1000. On the other hand, the degree of hydrolysis of the polymer is

not also specifically defined, but is preferably from 70 to 99 mol%, more preferably from 80 to 98 mol%, even more preferably from 83 to 95 mol%.

[0010]

Not interfering with the advantages of the invention, the polyvinyl alcohol may be a copolymer with any copolymerizable ethylenic unsaturated monomer. The ethylenic unsaturated comonomer includes, for example, acrylic acid, methacrylic acid, fumaric acid, maleic acid (anhydride), itaconic acid, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, trimethyl-(3-acrylamido-3-dimethylpropyl)-ammonium chloride, acrylamido-2-methylpropanesulfonic acid and its sodium salt, ethyl vinyl ether, butyl vinyl ether, vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride, vinylidene fluoride, tetrafluoroethylene, sodium vinylsulfonate, sodium allylsulfonate, N-vinylpyrrolidone, as well as N-vinylamides such as N-vinylformamide, N-vinylacetamide. Also usable herein are terminal-modified copolymers that are produced by copolymerizing a vinyl ester monomer such as vinyl acetate with  $\alpha$ -olefin in the presence of a thiol compound such as thiolacetic acid or mercaptopropionic acid, followed by hydrolyzing the resulting copolymer.

[0011]

In the invention, the dispersoid of the emulsion (A) comprises a polymer having one or more unsaturated monomer units

selected from ethylenic unsaturated monomers and dienic monomers. The ethylenic unsaturated monomers include, for example, olefins such as ethylene, propylene, isobutene; halogeno-olefins such as vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride; vinyl esters such as vinyl formate, vinyl acetate, vinyl propionate, vinyl versatate, vinyl pivalate; acrylic acid and acrylates such as methyl acrylate, ethyl acrylate, n-propyl acrylate, i-propyl acrylate, n-butyl acrylate, i-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, octadecyl acrylate; methacrylic acid and methacrylates such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, i-propyl methacrylate, n-butyl methacrylate, i-butyl methacrylate, t-butyl methacrylate, 2-ethylhexylmethacrylate, dodecylmethacrylate, octadecyl methacrylate; nitriles such as acrylonitrile, methacrylonitrile; allyl compounds such as allyl acetate, allyl chloride; styrene monomers such as styrene,  $\alpha$ -methylstyrene, p-methylstyrenesulfonic acid and its sodium and potassium salts; trimethyl(3-acrylamido-3-dimethylpropyl)ammonium chloride, 3-acrylamidopropyltrimethylammonium chloride, 3-methacrylamidopropyltrimethylammonium chloride, N-(3-allyloxy-2-hydroxypropyl)dimethylamine quaternary ammonium salt, N-(4-allyloxy-3-hydroxybutyl)diethylamine quaternary ammonium salt, as well as quaternary ammonium salts of acrylamide, N-methylacrylamide, N-ethylacrylamide,

N,N-dimethylacrylamide, diacetoneacrylamide,  
N-methylolacrylamide, methacrylamide, N-methylmethacrylamide,  
N-ethylmethacrylamide, N-methylolmethacrylamide; and  
hydroxypropyltrimethylammonium chloride methacrylate,  
hydroxypropyltrimethylammonium chloride acrylate,  
N-vinylpyrrolidone. The dienic monomers include, for example,  
butadiene, isoprene, chloroprene. One or more of these monomers  
may be used herein either singly or as combined.

Of the polymers that comprise any of the above-mentioned  
monomer units, preferred for use in the invention are polyvinyl  
esters such as typically polyvinyl acetate, and olefin-vinyl  
ester copolymers such as typically ethylene-vinyl acetate  
copolymer.

[0012]

The emulsion (A) for use in the invention may be obtained  
through emulsion polymerization of one or more monomers selected  
from ethylenic unsaturated monomers and dienic monomers in the  
presence of a polyvinyl alcohol having, in the molecule, from  
1 to 20 mol% of  $\alpha$ -olefin units with at most 4 carbon atoms; and  
the synthetic resin emulsion powder may be obtained by  
spray-drying the synthetic resin emulsion. In producing the  
synthetic resin emulsion, the initiator for the emulsion  
polymerization may be any ordinary polymerization initiator  
generally used in ordinary emulsion polymerization, for example,  
water-soluble initiators such as potassium persulfate, ammonium

persulfate, hydrogen peroxide, t-butyl hydroperoxide; oil-soluble initiators such as azobisisobutyronitrile, benzoyl peroxide. These may be used either singly or as a redox system combined with some reducing agent. The method of using it is not specifically defined. For example, it may be added to the polymerization system all at a time in the initial stage, or may be continuously added thereto.

[0013]

In the emulsion (A) for use in the invention, the amount of the polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units with at most 4 carbon atoms is not specifically defined. In general, it may be from 2 to 30 parts byweight, preferably from 3 to 15 parts byweight; more preferably from 4 to 10 parts by weight relative to 100 parts by weight of the monomer. If the amount of the polyvinyl alcohol is smaller than 2 parts by weight, the polymerization stability of the synthetic resin emulsion will be poor and, in addition, the mechanical stability and the chemical stability that are characteristic of the emulsion containing the polyvinyl alcohol as the dispersant thereof will lower and then the strength of the films formed of the resin emulsion will lower. If, on the other hand, the amount of the polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units with at most 4 carbon atoms is larger than 30 parts by weight, the viscosity of the polymerization system will increase, therefore causing

a problem of reaction heat removal. If so, in addition, the water resistance of the films formed of the resin emulsion will lower.

The mode of adding the polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units with at most 4 carbon atoms to the system is not specifically defined. It may be added thereto all at a time in the initial stage, or a part of it is added thereto in the initial stage and the remaining part thereof may be continuously added thereto during the polymerization.

If desired, any known nonionic, anionic, cationic or ampholytic surfactant or water-soluble polymer such as hydroxyethyl cellulose may be used along with the polyvinyl alcohol.

[0014]

Regarding the addition of the monomer in producing the emulsion (A) for use in the invention, employable are various methods. For example, the monomer may be added to the polymerization system all at a time in the initial stage; or a part of the monomer may be added thereto and the remaining part thereof may be continuously added thereto during the polymerization; or the monomer is previously emulsified with water along with a dispersant and the resulting emulsion may be continuously added to the polymerization system.

[0015]

If desired, a chain transfer agent may be added to the system in producing the emulsion (A) for use in the invention. Not specifically defined, the chain transfer agent may be any and every one that causes chain transfer in polymer. In view of the efficiency in chain transfer with it, preferred for use herein are mercapto group-having compounds. The mercapto group-having compounds are, for example, alkylmercaptans such as n-octylmercaptan, n-dodecylmercaptan, t-dodecylmercaptan; and 2-mercaptoethanol, 3-mercaptopropionic acid.

The amount of the chain transfer agent to be added to the system is preferably at most 5 parts by weight relative to 100 parts by weight of the monomer. If the amount of the chain transfer agent added is over 5 parts by weight, the polymerization stability of the synthetic resin emulsion produced will be poor and, in addition, the molecular weight of the polymer to form the dispersoid may greatly lower and, as a result, the physical properties of the emulsion may be thereby worsened.

[0016]

The synthetic resin emulsion powder of the invention may be obtained by spray-drying the emulsion (A). Spray-drying the emulsion may be effected in any ordinary manner of spraying and drying a liquid. Regarding the spraying mode for it, the emulsion may be sprayed with any of discs, nozzles or shock waves. For the heat source, employable is any of hot wind or hot steam. The drying condition may be suitably determined depending on



the size and the type of the spraying drier used, and on the concentration, the viscosity and the flow rate of the synthetic resin emulsion to be spray-dried. The drying temperature range suitably falls between 100°C and 150°C, within which it is desirable that the other drying conditions are determined so as to obtain well dried powder.

[0017]

For improving the storage stability and the redispersibility in water of the synthetic resin emulsion powder of the invention, it is desirable to add inorganic powder (antiblocking agent) to the emulsion powder. The inorganic powder may be added to the spray-dried emulsion powder and uniformly mixed with it. However, it is desirable that the synthetic resin emulsion (A) is sprayed in the presence of an inorganic powder (simultaneous spraying of emulsion along with inorganic powder) for more uniformly mixing them. Preferably, the inorganic powder is a fine powder having a mean particle size of from 0.1 to 100  $\mu\text{m}$ . For the inorganic powder, preferred is a powder of fine particles, for which, for example, usable are calcium carbonate, clay, silicic anhydride, aluminium silicate, white carbon, talc, and alumina white. Of those inorganic powders, more preferred is silicic anhydride. The amount of the inorganic powder is preferably at most 20 % by weight, more preferably at most 10 % by weight, in view of its properties. The lowermost limit of the amount is preferably

at least 0.1 % by weight, more preferably at least 0.2 % by weight.

As the case may be, a defoaming agent of silicone-based and/or hydrocarbon-based compounds may be added to the mixture being spray-dried.

[0018]

One preferred embodiment of the invention comprises adding a polyvinyl alcohol (B) to the emulsion (A) followed by spray-drying the resulting mixture to powder it. Adding a polyvinyl alcohol (B) further improves the redispersibility of the emulsion powder. Though not specifically defined, the amount of the polyvinyl alcohol (B) to be added may be generally from 1 to 50 parts by weight, but preferably from 2 to 30 parts by weight, more preferably from 3 to 20 parts by weight relative to 100 parts by weight of the solid content of the emulsion (A).

[0019]

The degree of polymerization of the polyvinyl alcohol (B) may be suitably determined in accordance with various conditions, not specifically defined. For easy operation to powder the emulsion, in general, it may be preferably from 100 to 3000, more preferably from 150 to 2000, even more preferably from 200 to 1600, most preferably from 200 to 1000. On the other hand, the degree of hydrolysis of the polyvinyl alcohol (B) is not also specifically defined, but is preferably from 70 to 99 mol%, more preferably from 80 to 97 mol%, even more preferably from 83 to 95 mol%.

[0020]

Not interfering with the advantages of the invention, the polyvinyl alcohol (B) may be a copolymer with any copolymerizable ethylenic unsaturated monomer. The ethylenic unsaturated comonomer includes, for example, olefins with at most 4 carbon atoms such as ethylene, propylene, butylene, isobutylene; acrylic acid, methacrylic acid, fumaric acid, maleic acid (anhydride), itaconic acid, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, trimethyl-(3-acrylamido-3-dimethylpropyl)-ammonium chloride, acrylamido-2-methylpropanesulfonic acid and its sodium salt, ethyl vinyl ether, butyl vinyl ether, vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride, vinylidene fluoride, tetrafluoroethylene, sodium vinylsulfonate, sodium allylsulfonate, N-vinylpyrrolidone, as well as N-vinylamides such as N-vinylformamide, N-vinylacetamide. Also usable herein are terminal-modified copolymers that are produced by copolymerizing a vinyl ester monomer such as vinyl acetate with the above-mentioned ethylenic unsaturated monomer such as ethylene in the presence of a thiol compound such as thiolacetic acid or mercaptopropionic acid, followed by hydrolyzing the resulting copolymer.

For the polyvinyl alcohol (B), preferred is a polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefins with at most 4 carbon atoms, preferably ethylene units, like

the polyvinyl alcohol that serves as the dispersant in the emulsion (A), since the polyvinyl alcohol (B) of the type further improves the redispersibility of the emulsion powder to be obtained, the dispersibility of the emulsion powder in hydraulic substances and the strength of the hardened constructions containing the polymer. For the polyvinyl alcohol (B), also preferred is a polyvinyl alcohol having a 1,2-glycol bond content of at least  $(1.7 - X/40)$  mol% where X (mol%) indicates the olefin unit content of the polymer and having from 1 to 20 mol% of  $\alpha$ -olefins, like the polyvinyl alcohol that serves as the dispersant in the emulsion (A), since the polyvinyl alcohol (B) of the type much more improves the redispersibility of the emulsion powder.

For adding the polyvinyl alcohol (B) to emulsion (A), for example, one preferred method comprises adding an aqueous solution of the polyvinyl alcohol (B) to an aqueous emulsion (A). Apart from it, also employable is a method of adding a powder, flakes or pellets of the polyvinyl alcohol (B) to emulsion (A). Still another method employable for it comprises adding the polyvinyl alcohol (B) to emulsion (A) being prepared through emulsion polymerization, all at a time or continuously, in the latter stage of emulsion polymerization to give the emulsion (A).

[0021]

The synthetic resin emulsion powder (having a mean particle

size of from 1 to 1000  $\mu\text{m}$ , preferably from 2 to 500  $\mu\text{m}$ ) may be directly used as an additive or joint material for hydraulic substances, but if desired, it may be combined with any other conventional known emulsion or emulsion powder not detracting from the advantages of the invention.

The hydraulic substances include, for example, hydraulic cement such as Portland cement, alumina cement, slag cement, fly ash cement; and other hydraulic materials than cement, such as gypsum and plaster.

[0022]

In case where the synthetic resin emulsion is added to cement mortar that comprises hydraulic material, aggregate and water, its amount is preferably from 5 to 20 % by weight of the hydraulic material. The aggregate may be any of fine aggregate such as river sand, ground sand, color sand and siliceous sand; and coarse aggregate such as river gravel and ground stones.

In case where the synthetic resin emulsion powder is used for a joint material for hydraulic substances, the powder is suitably redispersed in water and applied onto a hydraulic substance substrate of concrete or the like to be a joint material (primer-processing agent) for it, and then a hydraulic substance such as cement mortar is stuck onto it. Using the synthetic resin powder of the invention for such a joint material ensures good adhesiveness and good durability and even good mechanical strength of the bonded articles.

[0023]

For further improving the redispersibility of the synthetic resin emulsion powder in water, various water-soluble additives may be added to the emulsion powder. Preferably, the additives are added to the synthetic resin emulsion before the emulsion is spray-dried, and then the resulting mixture is spray-dried, to give uniform mixtures. Not specifically defined, the amount of the water-soluble additive to be in the resin emulsion powder may be suitably so controlled that it does not have any negative influence on the physical properties such as water resistance of the emulsion. The additives include, for example, hydroxyethyl cellulose, methyl cellulose, starch derivatives, polyvinylpyrrolidone, polyethylene oxide, as well as water-soluble alkyd resins, water-soluble phenolic resins, water-soluble urea resins, water-soluble melamine resins, water-soluble naphthalenesulfonic acid resins, water-soluble amino resins, water-soluble polyamide resins, water-soluble acrylic resins, water-soluble polycarboxylic acid resins, water-soluble polyester resins, water-soluble polyurethane resins, water-soluble polyol resins, water-soluble epoxy resins.

[0024]

Various additives may be added to the synthetic resin emulsion powder of the invention depending on the use of the emulsion powder. For example, when the emulsion powder is used

as an additive to mortar and cement, any of AE agent, water-reducing agent, fluidizing agent, water-retaining agent, thickener, waterproofing agent and the like may be added thereto; when it is used as an adhesive, any of viscosity improver, water-retaining agent, tackifier, thickener and the like may be added thereto; and when it is used as a paint binder, any of viscosity improver, thickener, pigment dispersant, stabilizer or the like may be added thereto.

[0025]

The invention is described concretely with reference to the following Examples; which, however, are not intended to restrict the scope of the invention. In the Examples, "part" and "%" are all by weight.

[0026]

[Examples]

Emulsion Production Example 1:

80 parts of aqueous 9.5 % solution of ethylene-modified PVA (PVA-1 having an ethylene unit content of 4 mol%, a degree of polymerization of 1300, and a degree of hydrolysis of 93 mol%) was fed into a pressure autoclave equipped with a nitrogen inlet mouth, a thermometer and a stirrer, heated up to 60°C, and then purged with nitrogen. 80 parts of vinyl acetate was fed into it, and then ethylene was into it to an increased pressure of 4.9 MPa. 2 g of aqueous 0.5 % hydrogen peroxide solution and 0.3 g of aqueous 2 % Rongalite solution were fed into it under

pressure, and the polymerization was then started. When the remaining vinyl acetate concentration reached 10 %, ethylene was discharged out until the ethylene pressure was lowered to 2.0 MPa. Then, 0.3 g of aqueous 3 % hydrogen peroxide solution was introduced into it under pressure to complete the polymerization. During the polymerization, no aggregation was found, and the polymerization stability of the system was good. The process gave ethylene-vinyl acetate copolymer emulsion (Em-1) having a solid concentration of 55 % and an ethylene content of 18 % by weight.

[0027]

#### Emulsion Production Example 2:

An ethylene-vinyl acetate copolymer emulsion (Em-2) having a solid concentration of 55 % and an ethylene content of 18.3 % by weight was produced in the same manner as in Emulsion Production Example 1, for which, however, an ethylene-modified PVA (PVA-2 having an ethylene unit content of 3 mol%, a degree of polymerization of 500, and a degree of hydrolysis of 95 mol%) was used in place of PVA-1 in Emulsion Production Example 1.

[0028]

#### Emulsion Production Example 3:

An ethylene-vinyl acetate copolymer emulsion (Em-3) having a solid concentration of 55 % and an ethylene content of 17.8 % by weight was produced in the same manner as in Emulsion Production Example 1, for which, however, an ethylene-modified



PVA (PVA-3 having an ethylene unit content of 5 mol%, a degree of polymerization of 1300, and a degree of hydrolysis of 98 mol%) was used in place of PVA-1 in Emulsion Production Example 1.

[0029]

#### Emulsion Production Example 4:

An ethylene-vinyl acetate copolymer emulsion (Em-4) having a solid concentration of 55 % and an ethylene content of 18 % by weight was produced in the same manner as in Emulsion Production Example 1, for which, however, a non-modified PVA (PVA-4 having a degree of polymerization of 1300, and a degree of hydrolysis of 93 mol%) was used in place of PVA-1 in Emulsion Production Example 1.

[0030]

#### Emulsion Production Example 5:

An ethylene-vinyl acetate copolymer emulsion (Em-5) having a solid concentration of 55 % and an ethylene content of 18.4 % by weight was produced in the same manner as in Emulsion Production Example 1, for which, however, a non-modified PVA (PVA-5 having a degree of polymerization of 500, and a degree of hydrolysis of 88 mol%, Kuraray's PVA-205) was used in place of PVA-1 in Emulsion Production Example 1.

[0031]

#### Emulsion Production Example 6:

An ethylene-vinyl acetate copolymer emulsion (Em-6) having a solid concentration of 55 % and an ethylene content

of 18.1 % by weight was produced in the same manner as in Emulsion Production Example 1, for which, however, a non-modified PVA (PVA-6 having a degree of polymerization of 1000, and a degree of hydrolysis of 98.5 mol%, Kuraray's PVA-110) was used in place of PVA-1 in Emulsion Production Example 1.

[0032]

Emulsion Production Example 7:

An ethylene-vinyl acetate copolymer emulsion (Em-7) having a solid concentration of 55 % and an ethylene content of 17.8 % by weight was produced in the same manner as in Emulsion Production Example 1, for which, however, an ethylene-modified PVA (PVA-7 having an ethylene unit content of 3 mol%, a 1,2-glycol bond content of 1.9 mol%, a degree of polymerization of 1300, and a degree of hydrolysis of 93 mol%) that had been prepared through high-temperature polymerization was used in place of PVA-1 in Emulsion Production Example 1.

[0033]

Emulsion Production Example 8:

An ethylene-vinyl acetate copolymer emulsion (Em-8) having a solid concentration of 55 % and an ethylene content of 17.9 % by weight was produced in the same manner as in Emulsion Production Example 1, for which, however, an ethylene-modified PVA (PVA-8 having an ethylene unit content of 5 mol%, a 1,2-glycol bond content of 2.2 mol%, a degree of polymerization of 500, and a degree of hydrolysis of 93 mol%) that had been prepared

through high-temperature polymerization was used in place of PVA-1 in Emulsion Production Example 1.

[0034]

Emulsion Production Example 9:

An ethylene-vinyl acetate copolymer emulsion (Em-9) having a solid concentration of 55 % and an ethylene content of 17.8 % by weight was produced in the same manner as in Emulsion Production Example 1, for which, however, an ethylene-modified PVA (PVA-9 having an ethylene unit content of 2.5 mol%, a 1,2-glycol bond content of 1.6 mol%, a degree of polymerization of 500, and a degree of hydrolysis of 88 mol%) was used in place of PVA-1 in Emulsion Production Example 1.

[0035]

Emulsion Production Example 10:

An ethylene-vinyl acetate copolymer emulsion (Em-10) having a solid concentration of 55 % and an ethylene content of 17.8 % by weight was produced in the same manner as in Emulsion Production Example 1, for which, however, an ethylene-modified PVA (PVA-10 having an ethylene unit content of 1.5 mol%, a 1,2-glycol bond content of 1.6 mol%, a degree of polymerization of 500, and a degree of hydrolysis of 88 mol%) was used in place of PVA-1 in Emulsion Production Example 1.

[0036]

Emulsion Production Example 11:

An ethylene-vinyl acetate copolymer emulsion (Em-11)

having a solid concentration of 55 % and an ethylene content of 17.8 % by weight was produced in the same manner as in Emulsion Production Example 1, for which, however, an ethylene-modified PVA (PVA-11 having an ethylene unit content of 0.5 mol%, a 1,2-glycol bond content of 1.6 mol%, a degree of polymerization of 500, and a degree of hydrolysis of 95 mol%) was used in place of PVA-1 in Emulsion Production Example 1.

[0037]

Emulsion Production Example 12:

Emulsion polymerization was tried in the same manner as in Emulsion Production Example 1, using an ethylene-modified PVA (PVA-12 having an ethylene unit content of 25 mol%, a 1,2-glycol bond content of 1.1 mol%, a degree of polymerization of 500, and a degree of hydrolysis of 95 mol%) in place of PVA-1 in Emulsion Production Example 1. In this, however, the system was unstable during emulsion polymerization, and it could not produce an emulsion.

[0038]

Emulsion Production Example 13:

5 parts of ethylene-modified PVA (PVA-1) and 90 parts of ion-exchanged water were fed into a glass vessel equipped with a reflux condenser, a dropping funnel, a thermometer, a nitrogen inlet mouth and a stirrer, and completely dissolved at 95°C. Next, its pH was made to be 4 with diluted sulfuric acid added thereto, and then 10 parts of methyl methacrylate, 10 parts of

n-butyl acrylate and 0.1 parts of n-dodecylmercaptan were added to it with stirring at 150 rpm. This was purged with nitrogen and heated up to 70°C. 5 parts of 1 % potassium persulfate was added to it to start the polymerization. Then, a mixture of 40 parts of methyl methacrylate, 40 parts of n-butyl acrylate and 0.4 parts of n-dodecylmercaptan was continuously added to it, over a period of 2 hours. 3 hours after the start of the polymerization, the conversion reached 99.2 %, and the polymerization was stopped in this stage. The process gave stable methyl methacrylate/n-butyl acrylate copolymer emulsion (Em-12) having a solid concentration of 51.5 %.

[0039]

#### Emulsion Production Example 14:

A methyl methacrylate/n-butyl acrylate copolymer emulsion (Em-13) having a solid concentration of 52 % was produced in the same manner as in Emulsion Production Example 13, for which, however, non-modified PVA (PVA-5) was used in place of PVA-1 in Emulsion Production Example 13.

[0040]

#### Emulsion Production Example 15:

5 parts of mercapto-terminated PVA (having an ethylene content of 0.5 mol%, a degree of polymerization of 550, a degree of hydrolysis of 88.3 mol% and a mercapto group content of  $3.3 \times 10^{-5}$  equivalent/g) (PVA-13) and 90 parts of ion-exchanged water were fed into a glass vessel equipped with a reflux condenser,

a dropping funnel, a thermometer, a nitrogen inlet mouth and a stirrer, and completely dissolved at 95°C. Next, its pH was made to be 4 with diluted sulfuric acid added thereto, and then 10 parts of methyl methacrylate, 10 parts of n-butyl acrylate and 0.1 parts of n-dodecylmercaptan were added to it with stirring at 150 rpm. This was purged with nitrogen and heated up to 70°C. 5 parts of 1 % potassium persulfate was added to it to start the polymerization. Then, a mixture of 40 parts of methyl methacrylate, 40 parts of n-butyl acrylate and 0.4 parts of n-dodecylmercaptan was continuously added to it, over a period of 2 hours. 3 hours after the start of the polymerization, the conversion reached 99.5 %, and the polymerization was stopped in this stage. The process gave stable methyl methacrylate/n-butyl acrylate copolymer emulsion (Em-14) having a solid concentration of 52.0 %.

[0041]

#### Emulsion Production Example 16:

An ethylene-vinyl acetate copolymer emulsion (Em-15) having a solid concentration of 55 % and an ethylene content of 17.8 % by weight was produced in the same manner as in Emulsion Production Example 11, for which, however, PVA (having a 1,2-glycol bond content of 1.9 mol%, a degree of polymerization of 1300, and a degree of hydrolysis of 93 mol%) (PVA-14) that had been prepared through high-temperature polymerization was used in place of PVA-1 in Emulsion Production Example 1.

[0042]

Example 1:

100 parts of the ethylene-vinyl acetate copolymer emulsion (A) (Em-1) obtained in Emulsion Production Example 1 was diluted with 50 parts of distilled water added thereto, and 2 %, relative to the solid content of the emulsion, of fine powder of silicic anhydride (having a mean particle size of 2  $\mu\text{m}$ ) were separately sprayed into hot air at 120°C at the same time and dried to obtain an emulsion powder having a mean particle size of 20  $\mu\text{m}$ .

[0043]

(Property Evaluation of Emulsion Powder)

100 parts of ion-exchanged water was added to 100 parts of the emulsion powder and well stirred in a stirrer, and this was evaluated for the following physical properties thereof. The results are given in Table 1.

- Redispersibility:

The redispersed emulsion was filtered through a 200-mesh stainless metal gauze filter, and the amount of the residue was measured.

- Condition after Redispersion:

The condition of the redispersed emulsion was observed with the naked eye and with an optical microscope, and evaluated according to the following criteria:

◎: The redispersion was uniform and had a mean particle size of not larger than 50  $\mu\text{m}$ .

O: The redispersion was uniform and contained no non-dispersed matter.

Δ: Though redispersed, the emulsion still contained non-dispersed matter.

x: Not redispersed.

• Film Formability:

The redispersion was cast on a glass plate at 50°C and dried, and its film formability was evaluated according to the following criteria:

O: A uniform film was formed, and it was tough.

Δ: A film was formed, but it was brittle.

x: No uniform film was formed.

• Property of Additive for Cement Mortar:

<1> Physical Test of Cement Mortar:

1) Mortar Composition:

Ratio by weight of solid content of aqueous emulsion/cement = 0.10;

Ratio by weight of sand/cement = 2.5;

Ratio by weight of water/cement = 0.5.

2) Slump value:

Measured according to JIS A-1173.

(This is an index indicating the dispersibility in cement mortar.)

3) Bending strength:

Measured according to JIS A-6203.



4) Compression strength:

Measured according to JIS A-6203.

[0044]

Examples 2 to 7, Comparative Examples 1 to 4:

Emulsion powders were produced in the same manner as in Example 1, for which, however, any of Em-2 to Em-11 prepared in Emulsion Production Examples 2 to 11 was used in place of Em-1 in Example 1. Also in the same manner as in Example 1, the physical properties of the emulsion powders thus obtained herein were measured and evaluated. The results are given in Table 1.

[0045]

Examples 8 to 10:

A mixture of 100 parts of the ethylene-vinyl acetate copolymer emulsion (A) (Em-1) that had been prepared in Emulsion Production Example 1 and a predetermined amount of aqueous 5 % solution of ethylene-modified PVA (B) (PVA-2), and 2 %, relative to the solid content of the emulsion, of fine powder of silicic anhydride were separately sprayed into hot air at 120°C at the same time and dried to obtain an emulsion powder. Its data are given in Table 1.

[0046]

Example 11, Comparative Examples 5 to 7:

Emulsion powders were produced in the same manner as in Example 1, for which, however, any of methylmethacrylate/n-butyl

acrylate copolymer emulsions (A) (Em-12, Em-13, Em-14, Em-15) prepared in Emulsion Production Examples 13 to 16 was used in place of Em-1 in Example 1. Also in the same manner as in Example 1, the physical properties of the emulsion powders thus obtained herein were measured and evaluated. The results are given in Table 1.

[0047]

**Example 12:**

A mixture of 100 parts of the methyl acrylate/n-butyl acrylate copolymer emulsion (A) (Em-12) that had been prepared in Emulsion Production Example 13 and 200 parts of aqueous 5 % solution of ethylene-modified PVA (B) (PVA-2), and 2 %, relative to the solid content of the emulsion, of fine powder of silicic anhydride were separately sprayed into hot air at 120°C at the same time and dried to obtain an emulsion powder. Its data are given in Table 1.

[0048]

Table 1

	Emulsion (A)					PVA (B)		film formability	Physical Properties of Mortar				
	PVA	ethylene modifier (mol%)	1,2-glycol content (mol%)	degree of polymerization	degree of hydrolysis (mol%)	amount (part)	filter residue		condition	slump (mm)	bending strength (kg/cm <sup>2</sup> )	compression strength (kg/cm <sup>2</sup> )	
Example 1	Em-1	PVA-1	4	1.5	1300	93	-	-	1.1	○	35	75	179
Example 2	Em-2	PVA-2	3	1.5	500	95	-	-	0.8	○	38	82	181
Example 3	Em-3	PVA-3	5	1.5	1300	98	-	-	4.5	○	33	70	175
Comp. Ex. 1	Em-4	PVA-4	0	1.6	1300	93	-	-	30	Δ	20	55	160
Comp. Ex. 2	Em-5	PVA-5	0	1.6	500	88	-	-	8	○	26	60	165
Comp. Ex. 3	Em-6	PVA-6	0	1.6	1000	98.5	-	-	76	×	-	-	-
Example 4	Em-7	PVA-7	3	1.9	1300	93	-	-	0.6	○	37	80	182
Example 5	Em-8	PVA-8	5	2.2	500	93	-	-	0.6	○	36	82	180
Example 6	Em-9	PVA-9	2.5	1.6	500	88	-	-	1.3	○	36	78	177
Example 7	Em-10	PVA-10	1.5	1.6	500	88	-	-	5	○	33	70	170
Comp. Ex. 4	Em-11	PVA-11	0.5	1.6	500	95	-	-	5.1	Δ	24	57	158
Example 8	Em-1	PVA-1	4	1.5	1300	93	PVA-2	10	0.5	○	36	80	225
Example 9	Em-1	PVA-1	4	1.5	1300	93	PVA-2	2	4.7	○	30	70	218
Example 10	Em-1	PVA-1	4	1.5	1300	93	PVA-2	25	3.2	○	31	72	220
Example 11	Em-12	PVA-1	4	1.5	1300	93	-	-	0.8	○	35	79	180
Comp. Ex. 5	Em-13	PVA-5	0	1.6	500	88	-	-	10	Δ	28	67	166
Example 12	Em-12	PVA-1	4	1.5	1300	93	PVA-2	10	0.6	○	36	80	233
Comp. Ex. 6	Em-14	PVA-13	0.5	1.6	550	88.3	-	-	6	○	29	61	160
Comp. Ex. 7	Em-15	PVA-14	0	1.9	1300	93	-	-	5.5	○	28	60	163

[0049]

[Advantages of the Invention]

The invention provides synthetic resin emulsion powder of good redispersibility. The redispersion of the resin emulsion powder well forms good films. When the powder is used as an additive to hydraulic substances, it well disperses in hydraulic substances and gives hardened constructions of high strength. When the powder is used as a joint material for hydraulic substances, it ensures good adhesiveness and durability and gives jointed hydraulic substances of high mechanical strength.

[Designation of Document]      Abstract

[Abstract]

[Problem] To obtain synthetic resin emulsion powder of good redispersibility. The redispersion of the resin emulsion powder well forms good films. When the powder is used as an additive to hydraulic substances, it well disperses in hydraulic substances and gives hardened constructions of high strength. When the powder is used as a joint material for hydraulic substances, it ensures good adhesiveness and durability and gives jointed hydraulic substances of high mechanical strength.

[Means for Resolution] A synthetic resin emulsion powder obtained by spray-drying an emulsion where the dispersant is a polyvinyl alcohol having, in the molecule, from 1 to 20 mol% of  $\alpha$ -olefin units with at most 4 carbon atoms and the dispersoid is a polymer having one or more unsaturated monomer units selected from ethylenic unsaturated monomers and dienic monomers; and an additive or joint material for hydraulic substances that comprises the powder.

[Drawing Selected] None.

***IN RE:* OPPOSITION TO EP-B-1420033**

**D3E**

## **Section 1 - Experimental Details**

Examples 21 and 22 of EP-A-1400557 were repeated.

Viscosity and T<sub>g</sub> values were measured.

## **Section 2 – Measurement of Viscosities**

Höppler viscosities (20°C, DIN53015) of 4% solutions of ethylene modified PVAs were measured. Results of the measurements are shown below in Table 3A.

Table 3A

	Ethylene Modified PVA			Höppler Viscosity (mPas) of 4% Solution of Ethylene Modified PVA
	Saponification (mol%)	Ethylene Content (mol%)	Polymerization	
Em.Pro.Ex. 21	93	4	1300	18.5
Em.Pro.Ex. 22	95	3	500	5.2

### Section 3 – Measurement of T<sub>g</sub> Values

T<sub>g</sub> of polymers (polyvinyl acetate) of emulsions were measured (DSC method). Results of the measurements are shown below in Table 3B.

Table 3B

	Ethylene Modified PVA			T <sub>g</sub> (°C)
	Saponification (mol%)	Ethylene Content (mol%)	Polymerization	
Em.Pro.Ex. 21	93	4	1300	3
Em.Pro.Ex. 22	95	3	500	2